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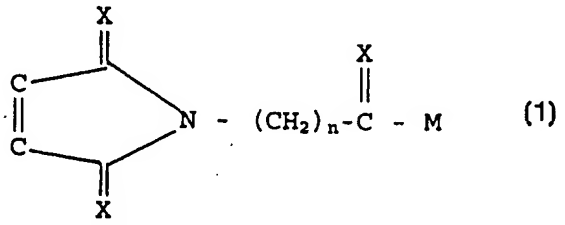
(54) Title: PROCESS FOR THE PREPARATION OF A MALEIMIDE COMPOUND, MALEIMIDE COMPOUND, RADIATION–CURABLE COMPOSITIONS COMPRISING SAID COMPOUND AND COATED PRODUCTS

(57) Abstract

The invention relates to a process for the preparation of a maleimide compound comprising the steps of (i) reacting a compound according to formula (1) wherein M is halogen or alkoxylate, and each X, independently, is O or S, with a compound (2) comprising a backbone and having at least 1 group per molecule, capable of reacting with the compound according to formula (1), and (ii) obtaining the maleimide compound.



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PROCESS FOR THE PREPARATION OF A MALEIMIDE COMPOUND, MALEIMIDE COMPOUND, RADIATION-CURABLE COMPOSITIONS COMPRISING SAID COMPOUND AND COATED PRODUCTS.

The invention relates to a synthetic route for making maleimide compounds. The invention further relates to certain maleimide compounds per se and to radiation curable compositions comprising said maleimide compounds. Finally, the invention relates to the coated products.

WO 98/07759 describes mono- and multifunctional aliphatic maleimides, photopolymerization methods using said maleimides and photopolymerizable compositions comprising said maleimides. WO 98/07759 also discloses the synthesis of several functionalized maleimide compounds derived from an hydroxy-functional compound (further called the OH-route). However, it appears that the synthesis of maleimides is generally cumbersome, several of these maleimide compounds are not easy to synthesise through the so-called OH-route and are therefore, not easy accessible. Only a few maleimide compounds are readily available.

Moreover, the maleimide compounds known from WO 98/07759 are all hydrocarbon substituted. However, hydrocarbon functional maleimide compounds appear to be not well compatible with other components that are generally used in radiation-curable composition.

With the aid of maleimide compounds it appears possible to induce photopolymerisation without the need of conventional photoinitiators or sensitizers, or, with a lower amount of photoinitiator.

Because most of the ethylenically unsaturated bonds of the maleimide are consumed during photopolymerisation, this photopolymerisation-inducing compound is built into the polymer network, and no residual maleimide based chromophores are left. Hence, the resulting radiation cured compositions are relatively stable, in particular with respect to light induced aging. Despite these potentially attractive characteristics, several disadvantages still are apparent. In particular, the maleimides described in the prior art are derived from N-methylol maleimide (N-hydroxymethyl maleimide) which is a very toxic compound. If the maleimide compound hydrolyses, this results in the release of the toxic alcohol compound. Furthermore, the maleimides described in the prior art exhibit a relatively slow cure.

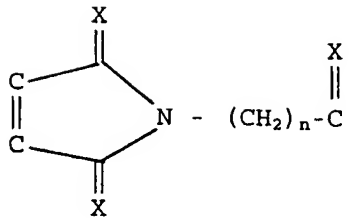
It is an object of the present invention to find a suitable and easier synthesis route to several maleimide compounds.

It is another object of the present invention to provide maleimide compounds that show an improved compatibility with the remaining components of the composition.

It is a further object of the invention to provide maleimide compounds that exhibit fast cure speed induction on photopolymerisation and a decreased amount of extractables.

One or more of these objects are achieved by a process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (1)



(1)

wherein M is halogen or alkoxylate, and each X, independently, is O or S,
with
a compound (2) comprising a backbone and having at least 1 group per molecule, capable of reacting with the compound according to formula (1), and
(ii) obtaining the maleimide compound.

The maleimide compound obtained by the process according to the present invention can be mono- or multifunctional.

The present invention provides an easy synthetic method for making a variety of mono- and multifunctional maleimide compounds. A further advantage of the synthetic method of the present invention is the great versatility, since the maleimide synthesis is performed before attachment to different backbones.

The unsaturated bond of the maleimide preferably is unsubstituted. However, the maleimide may be substituted with one alkyl or aryl group with 1-6 carbon atoms. Hence, the unsaturated bond of the maleimide in the formulae of this application can be denoted as HC = CR^4 wherein R^4 can be hydrogen or an alkyl or arylgroup with 1-6 carbon atoms. If both hydrogens would be alkyl groups, the cure speed severely lowers or, the maleimide compound does not polymerise due to steric hindrance. Hence, the

compounds depicted in the formulaes encompass the at one carbon atom substituted compounds.

In one particularly preferred embodiment X is oxygen and M is as defined above.

Suitable examples for M being a halogen are Cl, Br, and I; for M being an alkoxylate, examples include ethoxy, propoxy, t-butoxy, tert-butoxy carbonylate, substituted phenoxy and hydroxy succimide.

Preferably, the compound according to formula (1) is the acid-chloride functional maleimide-compound. The compound according to formula (1) for example is capable to react with compounds having hydroxy, thiol or amine functionality.

Compounds according to formula (1) can be obtained by suitable synthesis methods, for example such as described in L. Paul et al.; Chem. Ber. 100 2757-2760 (1967). However, this reference only describes the synthesis of a monofunctional maleimide compound (with 1 methylene between the maleimide group and the functional group) via the reaction between an acid chloride functional maleimide compound and an aminophenyl. However, the present invention is directed to maleimide compounds (ii), with the exception of a monofunctional maleimide compound having an aromatic amine as functional group, because aromatic amine groups include yellowing.

The reaction between the compound according to formula (1) and the compound (2) is preferably performed at a temperature range between -30°C and +80°C in (a suitable) organic solvent such as tetrahydrofuran, dichloromethane, pyridine, diethylether, toluene, esters, carbonates and the like. The reaction can also be performed in mixtures of the

above mentioned organic solvents. Preferably, ester-based organic solvents are used, such as dimethylcarbonate, which increases the yield of the reaction. In another preferred embodiment, the reaction of the acid chloride functionalised maleimide with hydroxy functional groups is performed in equimolar amounts of tetrahydrofuran and pyridine below 0°C.

Further, hindered phenol-type stabilisers preferably are added to the reaction mixture to avoid polymerisation of the maleimide group at elevated temperatures. Preferably, t-butyl catechol is used as stabiliser.

Moreover, the reaction generally is performed in the absence of water and in the presence of base.

The present process can be used to synthesise mono- and multifunctional maleimides.

First, there are several preferred embodiments for the preparation of the monofunctional maleimide compounds according to the present invention.

One of the preferred embodiments according to the present invention is directed to the process for the preparation of monofunctional maleimide compounds wherein n equals 1 and wherein the backbone is not comprising benzophenone, a succinimide or phenyl group.

Another preferred embodiment of the process according to the present invention is the preparation of monofunctional maleimide compounds wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 169 and is not comprising an anhydride or cyclodextrine group.

Second, there are several preferred embodiments for the preparation of the multifunctional

maleimide compounds according to the present invention.

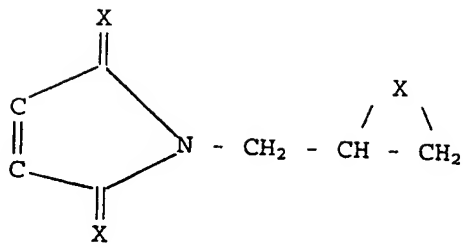
Multifunctional aliphatic maleimide compounds are known as such from WO-A-98/11141, EP-A-241133 and EP-A1-878482. Both synthesis methods suffer from a lack of versatility in making a large variety of compounds. Also, maleic and fumaric amid acids will be present due to incomplete imidisation. However, the products obtained by the process according to the present invention contain maximum 6 wt.% of impurities such as not ring-closed maleimide by-products. Therefore, our technique results in an improved combination of purification and % yield.

One of the preferred embodiments according to the present invention is directed to the process for the preparation of multifunctional maleimide compounds wherein n equals 1. The hydrogens of the CH_2 group next to two non-aliphatic groups are relatively labile, thereby increased cure speed is caused.

Another preferred embodiment of the process according to the present invention is the preparation of multifunctional maleimide compounds wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 150 and does not comprise a nitrogen containing phenyl group.

Another synthetic pathway for making mono- and multifunctional maleimide compounds according to the present invention is a process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (3)



(3)

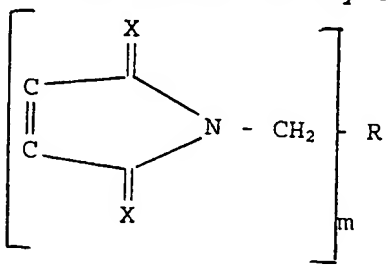
wherein X, independently, is O or S,
with
a compound (4) having at least on average 1 group per molecule, capable of reacting with the compound according to formula (3) and

(ii) obtaining the maleimide compound.

The compound according to formula (3) for example is capable of reacting with carboxylic acid, hydroxy, thiol, phosphine, amine and phosphoric acid functionality.

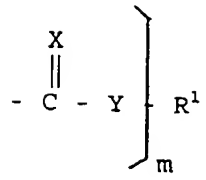
Compounds according to formula (3) can be obtained by suitable synthesis methods, for example such as described in T. Kurosaki et al.; J. Phot. Sc. 36 122-124 (1988).

Maleimide group comprising compounds according to the invention and examplified by formula (3) appear to be very efficient for the induction of photopolymerisation of for example (meth)acrylates, even in the absence of any other photoinitiator:

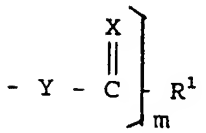


(5)

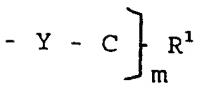
wherein R is



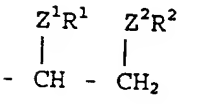
(5.1)



(5.2)



(5.3)



(5.4)

wherein

m is at least 1,

each X, independently, is O or S

Y is O, S or NH

Z^1 and Z^2 independently designate for O, S, or NR^3, and wherein R^1, R^2 and R^3 can be, independently, hydrogen or an organic group and wherein R^1, or at least R^1 or R^2 is the remainder of the backbone of the multifunctional maleimide compound.

In one particularly preferred embodiment X is oxygen and Y is as defined above. Most preferably, Y is O or NH; and R' is the remainder of the molecule.

The maleimide groups are attached via the functional group to the remainder of the molecule (R', R^1 or R^2), further in this application also called the backbone.

The backbone (R', R^1 or R^2) can be any suitable organic molecule. In particular, a distinction can be made between two classes of organic molecules/backbones.

A first class of backbones are reactive backbones; in particular, these backbones comprise one or more groups that are reactive in the photopolymerisation process. The active site of such group can be a photoinitiating molecule, a co-initiator or sensitizer, a polymerizable, ethylenically unsaturated group, and the like. Suitable examples of the active sites are benzophenone, thioxanthone, an aliphatic tertiary amine, a (meth)acrylate, a vinylether and the like. Most preferably, no aromatic amines are used. Maleimide compounds with an aromatic amine group have a tendency to yellow.

A second class of organic backbones comprises molecules that are non-reactive towards the photopolymerisation process. The non-reactive backbone molecule can be of low or high molecular weight. The molecular weight of the non-reactive groups will generally be higher than 14 and lower than 90,000. Preferably, the molecular weight will be higher than 50 and lower than 50,000. Most preferably, higher than 100 and lower than 10,000. This class comprises lower molecular weight groups such as methyl, ethyl, propyl, isopropyl, butyl, tert-butyl, cyclohexyl, phenyl, bisphenyl, substituted phenyl and the like. Moreover, the higher molecular weight groups can be any organic groups such as hydrocarbons, oligoesters, oligoethers, oligocarbonates, oligourethanes, oligoimides, oligoamides, oligoacrylates and the like. The term "oligo" refers to oligomers having at least two repeating units and includes also the "poly"mers.

Suitable backbone molecules of the monofunctional maleimide compounds can be derived from hydroxy or aminofunctional molecules such as, for example, from trimethylolpropane diacrylate,

pentaerythritol triacrylate, monohydroxy functional polyethyleneglycol, monohydroxy functional polypropyleneglycol, mono-amino functional polyethers, available as Jeffamine®, hydroxy acids and the like.

Suitable backbone molecules for the multifunctional maleimide compounds can be derived from hydroxy or aminefunctional molecules such as, for example, from trimethylolpropane, pentaerythritol, dipentaerythritol, amine functional dendrimers like Astramol®, polyethyleneglycol, polypropylene-glycol, amine functional polyesters, available as Jeffamine®, acid or hydroxyfunctional polyesters derived from diols, diacids and/or hydroxy acids, acid, amino or hydroxyfunctional acrylic polymers, isophorone diisocyanate, toluene diisocyanate, and trimerisation products therefrom, polycarbonate-diols, and the like.

Preferred backbone molecules are polyethers, ethoxylated compounds, and polyurethanes. In particular, trimethylol propane, ethoxylated trimethylol propane, propoxylated trimethylol propane, pentaerythritol, ethoxylated pentaerythritol, glycerol, propoxylated glycerol, polytetrahydrofuran, polyethylene oxide, polypropylene oxide, and tert-amine bearing backbones.

The molecular weight of the maleimide compound (ii) will generally be higher than 159 and lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable composition. The molecular weight as used herein is (for oligomeric compounds) the number average molecular weight, as determined by Gel Permeation Chromatography (GPC) with polystyrene standards.

The number of maleimide groups per molecule can vary from one up to 20, preferably from 1 up to 10, more preferred from 1 up to 5.

The number of carbon atoms n between the maleimide and the carbonyl can be 1, 2 or higher. Generally, n will be lower than 20, preferably lower than 10. The alkylene group is aliphatic, and preferably is a straight chain alkylene, but it may comprise a cyclic group. Suitable examples include ethylene, 1,3-propylene, 1,2-propylene, methylcyclohexylene, 1,3-t-butylene, 1,5-pentylene and the like. Compounds with maleimide functional groups with only one methylene carbon spacer between a functional group and the maleimide chromophore are particularly cumbersome to synthesise.

The maleimide compound according to this invention preferably has an ester, thioester, carbonate, ether, urethane, amine, amide or imide as the functional group. Most preferably, an ester functional group.

In one preferred embodiment of the maleimide compound of the invention, the maleimide compound according to formula (5) is monofunctional (m=1).

The molecular weight of the monofunctional maleimide compound will generally be higher than 159, preferably higher than 173 and in particular higher than 250. Higher molecular weight maleimide compounds are generally better compatible with the other constituents of the radiation curable coating composition. However, low molecular weight compounds can be made compatible by varying the R-group functionality.

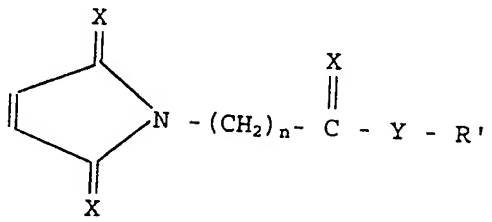
The molecular weight of the monofunctional

maleimide compound generally will be lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable composition. Preferably, the molecular weight will be lower than 10,000, more preferably, lower than 5000, and particularly preferred below about 1000 because such molecular weights make it more easy to formulate radiation curable compositions without non-reactive diluents.

The monofunctional maleimide compound according to this invention preferably has an ester, thioester, ether, amide, imide or amine as the functional group. More preferably, an ester, thioester or amide functional group, most preferably, an ester functional group.

Monofunctional maleimide compounds according to formula (5), with the exception of R' being an aromatic amine, are novel.

Preferred monofunctional maleimide compounds are compounds according to formula (6)



(6)

wherein Y is O, S or NH;
each X, independently, is O or S; and
R' is the remainder of the backbone, and wherein

(i) n equals 1 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and not comprising benzophenone, a succinimide or anhydride group, or

(ii) n equals 2 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and said backbone is not comprising a diol-substituted alkane, a succinimide, anhydride or cyclodextrine group, or

(iii) n is at least 3.

In a second preferred embodiment of the maleimide compound of the invention, the maleimide compound according to formula (5) is multifunctional (m>1).

Preferably, the multifunctional maleimide compound has a functionality of 1.9 or higher, in particular 2.5 or higher, as a higher functionality appears to improve cure speed and to give cured products with lower photoinitiator based extractables.

The upper limit of the functionality seems to be non-critical, and the functionality will be in general lower than 20, preferably lower than 10 and in particular will be about 5 or lower.

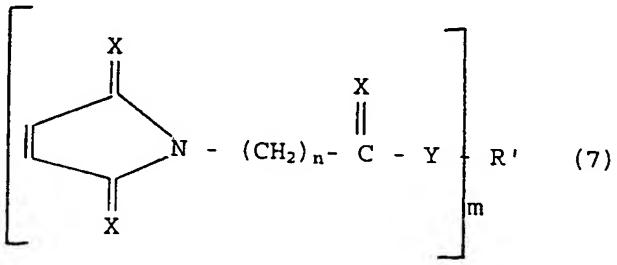
The molecular weight of the multifunctional maleimide compound will generally be higher than 250, preferably higher than 325 and in particular higher than 400. The molecular weight of the multifunctional maleimide compound generally will be lower than about 100,000, although the upper limit is not critical, and will be mainly determined by viscosity limitations of the radiation curable composition. Preferably, the molecular weight will be lower than 50,000, more preferably lower than 10,000, particularly preferred below about 10,000 and most preferred below about 5,000 because such molecular weights make it more easy to formulate radiation curable compositions without non-reactive diluents.

The multifunctional maleimide compound

according to this invention preferably has an ester, thioester, carbonate, ether, urethane, amine, amide or imide as the functional group. Most preferably, an ester functional group.

Multifunctional compounds according to formulaes (5) are novel, excluding phenolic group comprising backbones for formula (5.4).

Preferred multifunctional maleimide compounds are compounds according to formula (7)



(7)

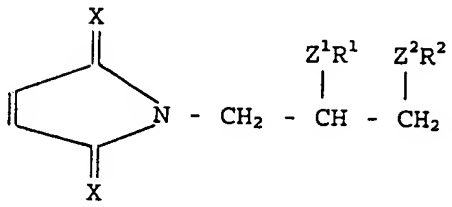
wherein each X, independently, is O or S,
Y is O, S or NH,
R' is the remainder of the backbone, and m is - on average - 1.6 or higher, and wherein

(i) n equals 1 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

(ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent

carbons.

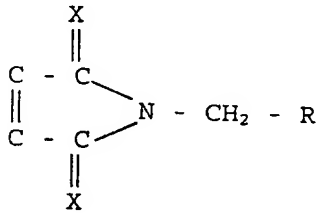
Furthermore, the present invention also relates to maleimide compounds according to formula (8)



(8)

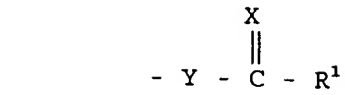
comprising at least one maleimide group, wherein X is O or S, and Z^1 and Z^2 independently designate for O, S, or NR^3, and wherein R^1, R^2 and R^3 can be, independently, hydrogen or an organic group and wherein at least R^1 or R^2 is the remainder of the molecule. The maleimide compounds according to formula (8) can be mono- or multifunctional.

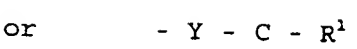
Other preferred multifunctional maleimide compounds are the ones depicted by formula (9)



(9)

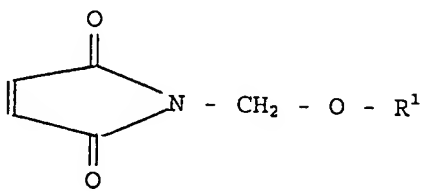
wherein R is



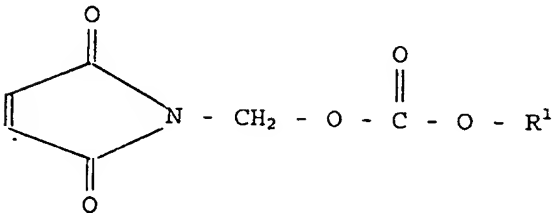
or 

wherein
each X, independently, is O or S
Y is O, S or NH, and
wherein R^1 is the remainder of the backbone of the multifunctional maleimide compound.

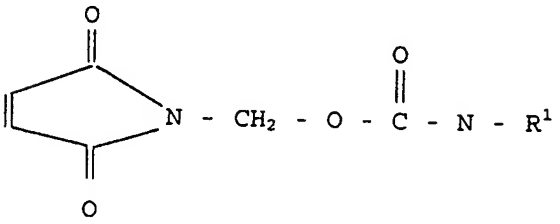
Especially preferred are the ones wherein X and Y are O and are depicted by formulaes (10) to (12)



(10)



(11)



(12)

Further, the present invention relates to a radiation-curable composition comprising

a) at least one compound having ethylenically

unsaturated bonds other than those in maleimide groups as defined under (b)

b) at least one maleimide compound according to formula (6), (7) or (8) wherein

Y is O, S or NH,
each X, independently, is O or S,
m is - on average - 1.6 or higher,
R' is the remainder of the molecule,
Z^1 and Z^2 independently designate for O, S, or NR^3, and wherein R^1, R^2 and R^3 can be, independently, hydrogen or an organic group and wherein at least R^1 or R^2 is the remainder of the molecule.

In one preferred embodiment of the radiation curable composition according to the present invention, the monofunctional maleimide compound according to formula (6) is further characterised by

(i) n equals 1 and R' is an organic backbone being non-reactive towards the photopolymerization process, said backbone comprising hydrogen, carbon and at least one of O, S, or N, and not comprising a succinimide or anhydride group, or

(ii) n equals 2 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and said backbone is not comprising a diol-substituted alkane, a succinimide, anhydride or cyclodextrine group, or

(iii) n is at least 3.

In a second preferred embodiment of the radiation curable composition according to the present invention, the multifunctional maleimide compound according to formula (7) is further characterised by

(i) n equals 1 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)carbonate, (oligo)urethane,

(oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

(ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons.

In a third preferred embodiment of the radiation curable composition according to the present invention, the maleimide compound according to formula (8) is further characterised by comprising at least one maleimide group.

The present invention also relates to radiation-curable composition comprising

a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)

b) at least one multifunctional maleimide compound having at least 2 maleimide groups according to formula (9).

Preferably, the radiation curable composition according to the present invention comprises a maleimide compound (b) as defined above wherein X is oxygen.

The maleimide compound preferably is present in the radiation curable composition in an amount between 0.01-60 wt.%. More preferably, the monofunctional maleimide compound is present in the radiation curable composition between 0.1-50 wt.%, most

preferably between 0.1-20 wt.%.

More preferably, the multifunctional maleimide compound is present in the radiation curable composition in an amount between 0.1-20 wt.%.

Generally, the amount of maleimide groups is such, that the ratio of maleimide groups to other ethylenically unsaturated groups is 0.001 or higher, preferably 0.01 or higher. Generally, the amount of maleimide groups is 1 or lower with respect to the other ethylenically unsaturated groups, preferably 0.5 or lower and particularly preferred 0.2 or lower.

The radiation curable composition comprises

a) at least one compound having ethylenically unsaturated bonds other than those in the maleimide groups of (b), and

b) the maleimide compound, being mono- or multifunctional.

The radiation curable composition of the present invention comprises (a) and (b); for purposes of definition of wt. amounts, the total amount of (a) + (b) is 100 wt.%, and additional compounds that can be present are defined relative to the amount of (a) + (b).

Both compounds (a) and (b) can be mixtures of compounds.

Examples of the ethylenically unsaturated group of compound (a) include (meth)acrylate, propenylether, vinylether, allylether, substituted or unsubtituted styrene, N-vinyl, fumarate, maleate, itaconate, (meth)acrylamide, and mixtures of these.

Preferred ethylenically unsaturated groups are (meth)acrylate, N-vinyl, styrene and vinylether. Most preferred are (meth)acrylate functional compound.

The compound (a) preferably is a mixture of

oligomers and reactive diluents. Also preferred is a mixture of monofunctional and multifunctional compounds.

Examples of suitable oligomers comprise (meth)acrylated polyesters, (meth)acrylated urethanes, (meth)acrylated epoxies, vinyl-ether functional urethanes and the like.

Examples of suitable reactive diluents are lauryl(meth)acrylate, ethyl(meth)acrylate, ethoxyethyl(meth)acrylate, phenoxyethyl(meth)acrylate, hexanedioldi(meth)acrylate, triethyleneglycol divinylether, trimethylol propanetri(meth)acrylate, isobornyl(meth)acrylate, N-vinyl-caprolactone, diethyleneglycol di(meth)acrylate, cyclohexyldimethanol-di(meth)acrylate and the like.

In one embodiment of the invention, the radiation curable composition comprises electron rich and electron poor double bonds, as described in EP-A-618237 and WO97/31981.

In another preferred embodiment, the composition comprises only electron-poor double bonds such as acrylates, fumarate compounds and the like.

The compositions comprising (a) and (b) are radiation curable as such. Nevertheless, cure speed can be further improved using type-II (hydrogen abstraction) photoinitiators such as benzophenone, derivatives of benzophenone, such as substituted benzophenone, xanthone, thioxanthone, substituted thioxanthone and other xanthone derivatives, anthraquinones, coumarines, in an amount between 0.1-10 wt.% (with respect to (a) + (b)). Type-II photoinitiators generally are used with an amine synergist. When using compound (b) according to the present invention, amine synergists are not necessary

in particular if curing is performed under a nitrogen atmosphere. Hence, preferable, amine synergists are present in an amount of less than 1 wt.%, and more preferably less than 0.1 wt.%. Nevertheless, amine synergist can be used up to 5 wt.% if useful in particular if curing is performed under an oxygen containing atmosphere, like in air.

Other examples of suitable photoinitiators are type I (α-cleavage) photoinitiators such as Darocure 1173 (2-hydroxy-2-methyl-1-phenylpropane-1-one as the active component), Irgacure 184 (hydroxy-cyclohexyl phenyl ketone as the active component), Irgacure 369 (2-benzyl-2-dimethylamino-1-(morpholinophenyl)-butanone-1 as the active component), and acylphosphines such as Lucerin TPO (2,4,6-trimethylbenzoyl diphenyl phosphine oxide). Chemical derivatives and combinations of these photoinitiators can also be used.

The radiation curable compositions can further comprise usual additives, colorants, fillers and the like, such as for example pigments, flow agents, stabilisers, antioxidants, slip agents, waxes, dyes, wetting agents, adhesion promotors, and the like.

The radiation-curable coating composition can be cured by different kinds of radiation, such as UV and EB radiation.

The most preferred irradiation source is ultraviolet light. Ultraviolet light is preferably high intensity light to provide a dosage to achieve reasonable curing rates. In the event that lower energy light is applied, it may then be desired to subject the compositions also to elevated temperatures in order to reduce the time for adequate polymerisation to occur.

With respect to UV-curing equipment we refer to, for example, pages 161-234 of Chemistry and Technology of UV and EB-formulations, Volume 1, Oldring 1991.

Suitable lamps employed to provide the desired high intensity and availablitiy of wavelength and spectral distribution include for example those available from Fusion Systems, Corp. Preferably, excimer lamps are used e.g. Fusion VIP 308.

The radiation-curable coating composition according to the invention can be used on different substrates, for example glass, paper, wood, plastic, metals such as aluminium and iron. An example of a glass substrate can be an optical glass fiber.

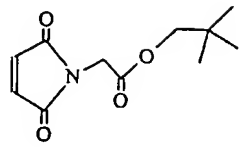
Finally, the present invention also relates to the products coated with a cured coating which coating before curing is a coating composition as described herein.

The invention will be elucidated with the following examples, without being limited thereto.

Examples I-VI are related to the preparation and characterisation of monofunctional maleimide compounds with 1 methylene spacer group between the maleimide group and the functional group. Further, the use of said maleimides in the preparation of a radiation-curable composition is described.

Example I

Preparation of a monofunctional maleimide compound from neopentyl alcohol:

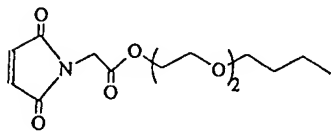


60 mmol 2,2-dimethyl-1-propanol and 60 mmol triethylamine were dissolved in 100 ml dry tetrahydrofuran. The mixture was cooled to 0C and 84 mmol N-[(chloroformyl)methyl]maleimide dissolved in 50 ml tetrahydrofuran was slowely dropped to the solution. The reaction mixture was stirred overnight at room temperature. After filtration and evaporation, the brownish residu was dissolved in 150 ml dichloromethane and washing with 60 ml 10% HCl and further washing three times with 60 ml water. Drying on sodiumsulfate, filtration and evaporation yielded a yellow powder. After drying in a vacuum oven 42 mmol (73%) of a light yellow powder was obtained.

The structure was characterised by:
^{1}H-NMR ($CDCl_3$) (δ/ppm): 6.8 (s, 2H); 4.3 (s, 2H); 3.85 (s, 2H); 0.95 (s, 9H)
IR, neat (frequency cm-1): 1715 (C=O maleimide); 697 (C-H bend of maleimide double bond)

Example II

Preparation of a monofunctional maleimide compound from butyl carbitol:



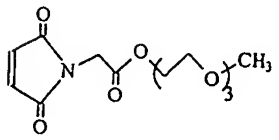
6.8g (42mmol) 2-(2-butoxyethoxy)ethanol was dissolved in 150ml THF. 7.0ml (50mmol) triethylamine and tert-butyl catechol were added. [In the synthesis examples, generally, between about 10 and about 50 mg of tert-butyl catechol is used.] The solution was cooled to -10°C and stirred thoroughly.

8.0g (46mmol) N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise in one hour. The reaction was stirred overnight at room temperature and filtered off. The clear brown filtrate was evaporated till an oil was obtained. Dissolving in dichloromethane and washing with water yielded 7.25g (24mmol, 57%) of a brown/orange oil.

^{1}H-NMR, $CDCl_3$ (δ/ppm): 6.75(s,2H); 4.25(t,4H); 3.55(3t, 8H); 1.5(m,2H); 1.3(q,2H); 0.85(t,3H)
IR, neat (frequency cm^{-1}): 1718(C=O maleimide); 698 (C-H bend of maleimide double bond)

Example III

Preparation of a monofunctional maleimide compound from triethylene glycol monomethyl ether:



6.5g (40mmol) triethylene glycol monomethyl ether was dissolved in 100ml THF. 5.75ml (41mmol) triethylamine and tert-butyl catechol were added. The solution was

cooled down to -10°C and 7.0g (40mmol) of N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added in 30 minutes. After stirring overnight at room temperature, filtration and evaporation of the THF, the dark liquid was dissolved in dichloromethane and washed three times with water. The product was collected as a orange/yellow oil with a yield of 6.8g (22.5mmol, 56%).

^{1}H-NMR, $CDCl_3$ (δ/ppm): 6.8(s,2H); 4.3(t,4H); 3.65(m&t,10H); 3.9(s,3H)

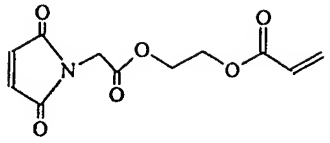
Example IV

Preparation of a monofunctional maleimide compound from 4-aminobenzophenone:

To a solution of 55mmol 4-aminobenzophenone in 250ml THF, tert-butyl catechol and 60mmol triethylamine were added. The solution was cooled down to -10°C. 55mmol N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. The reaction was stirred at room temperature overnight and filtered off. The filtrate was then evaporated and a solid product was obtained. After washing with water and diethylether, the product was dried under vacuum. This yielded 48mmol (87%) of a white powder.

Example V

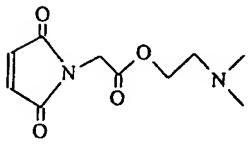
Preparation of a monofunctional (acrylate functional) maleimide compound from 2-hydroxyethyl acrylate:



To a 0°C solution of 5.75ml (50mmol) 2-hydroxyethyl acrylate, tert-butyl catechol and 7.0ml (50mmol) triethylamine 8.7g (50mmol) N-[(chloroformyl) methyl] maleimide dissolved in 50ml THF was added dropwise. The reaction was stirred at room temperature overnight. Fitration and extraction with CH_2Cl_2/H_2O yielded an orange oil which turns to solid in an ice/water bath. 3.0g (11.8mmol, 23%) of a light yellow/pale white powder was obtained by crystallisation from cold ether.

Example VI

Preparation of a monofunctional maleimide compound from dimethyl ethanolamine:



4.9g (55mmol) dimethyl ethanolamine and tert-butyl catechol were dissolved in 200ml CH_2Cl_2 and cooled down to 0°C. 9.6g (55mmol) N-[(chloroformyl) methyl] maleimide dissolved in 40ml dichloromethane was added dropwise. The suspension was stirred overnight at room temperature and quenched with 2.17g (54mmol) $NaOH_{(aq)}$. Separation of the water layer and washed with water yielded a red thick oil.

Preparation of a radiation curable composition comprising a monofunctional maleimide of Ex. I or IV:

A radiation curable composition was prepared by mixing 1 wt.% of the compound X in Table 1 with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% of an tetrafunctional polyester acrylate oligomer (Ebecryl®80 from UCB).

A coating was applied on a glass substrate using a variable thickness doctor blade, wire wound applicator (e.g. 200 µm 'K-bar') and the coating was cured by UV light (N_2, 2.2 J/cm^2), using a Fusion H-bulb lamp (6 kW).

Table 1:

composition comprising maleimide from	König hardness (s)
(Example I)	63.0
(Example IV)	71.4

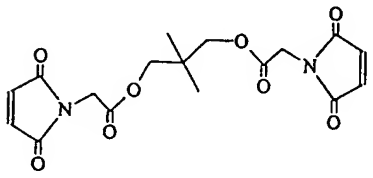
These data show that the presence of a monomaleimide compound in a coating composition results in a radiation-curable coating, which is properly cured upon radiation.

Examples VII to XX are related to the preparation and characterisation of multifunctional maleimide compounds with 1 methylene spacer group between the maleimide group and the functional group.Further, the use of said

maleimides in a radiation-curable composition comprising said maleimides is given.

Example VII

Preparation of a bis-maleimide from 2,2-dimethylpropanediol



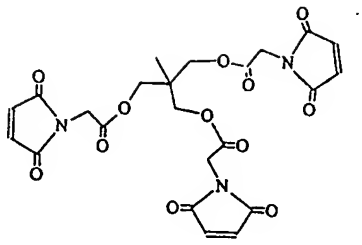
3.15g (30.2mmol) 2,2-dimethylpropanediol was dissolved in 75ml THF, 5.0ml (64mmol) pyridine (and tert. butyl catechol) were added. [In the synthesis, generally about 10-50 mg tert. butyl catechol was used]. After cooling down to -10°C 10.5g (60.5mmol) N-[(chloroformyl)methyl] maleimide dissolved in 75ml THF was added slowly to the solution. After stirring overnight, filtration, extraction with water/ether, drying, decoloring and evaporation an orange oil was collecter. The orange oil became a wet solid after adding ether.

After crushing and drying in a vacuumoven 3.45g (9mmol, 30%) of a white/light yellow solid was obtained.

^{1}H-NMR CDCl$_3$ (δ/ppm): 6.8(s,4H); 4.3(s,4H); 3.9(s,4H); 0.95(s,6H)

Example VIII

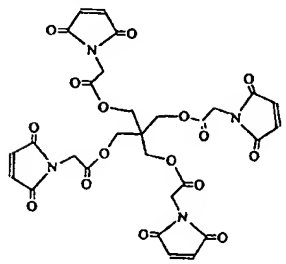
Preparation of a tris-maleimide from tris-(hydroxymethyl)ethane



To 1.80g (15mmol) 1,1,1-tris(hydroxymethyl)ethane dissolved in 100ml THF 6.5ml (46mmol) triethylamine and tert. butyl catechol were added. After cooling to -10°C 8.0ml (46mmol) N-[(chloroformyl) methyl] maleimide dissolved in 50ml THF was added dropwise. After stirring for three hours at room temperature the reaction mixture was filtered off, evaporation of the orange filtrate yielded a sticky solid which was suspende in ether. After fitration, washing with ether/water and drying in the vacuumoven 6.8g (12.8mmol, 85%) of a pale white powder was obtained . *^{1}H-NMR $CDCl_3$* (δ/ppm): 6.76(s,6H); 4.25(s,6H); 3.95(s,6H); 0.95(s,3H)

Example IX

Preparation of a tetra-maleimide from pentaerytriol

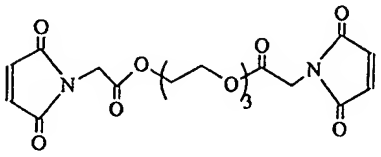


2.72g (20mmol) pentaerythriol, tert. butyl catechol and 25ml (180mmol) triethylamine were dissolved in 75ml

THF. After cooling to -10°C 14.5gram (84mmol) N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. After stirring overnight at room temperature the brown suspension was quenched with water and filtered off. The brown residu contained the amine salt as well as the desired product. Several washings with water and drying in the vacuumoven yielded 5.5g (8mmol, 40%) pale white/brownish powder.
^{1}H-NMR, dmso-d6 (δ/ppm): 7.15(s,2H); 4.3(s,2H); 4.1(s,2H);
melting point: 162-165°C

Example X

Preparation of a bis-maleimide from triethyleneglycol

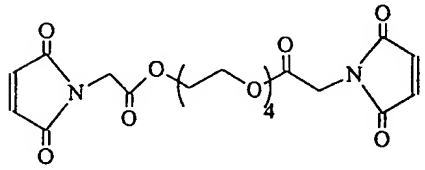


7.5g (50mmol) triethyleneglycol was dissolved in 150ml dimethylcarbonate. 14.0ml (100mmol) triethylamine and tert. butyl catechol were added while the mixture was cooled to 0°C. 17.4g (100mmol) of N-[(chloroformyl)methyl] maleimide dissolved in 50ml dimethylcarbonate was added dropwise. After the reaction was stirred overnight at room temperature it was filtrated off and the filtrate was evaporated. The oil which was obtained crystallised after the addition of ether (150 ml) 15.2grams (35.8mmol, 72%) of a yellow powder was obtained. When repeating this experiment with 50% higher amounts, a yield was obtained of 80%.

^{1}*H-NMR, CDCl$_3$* (δ/ppm): 6.8(s,4H); 4.3(d,8H); 3.7(q,8H)
^{13}*C-NMR CDCl$_3$* (δ/ppm): 135(C=C); 78.5(t, quart. C); 68.5(t,CH_2);

Example XI

Preparation of a bis-maleimide from tetraethyleneglycol

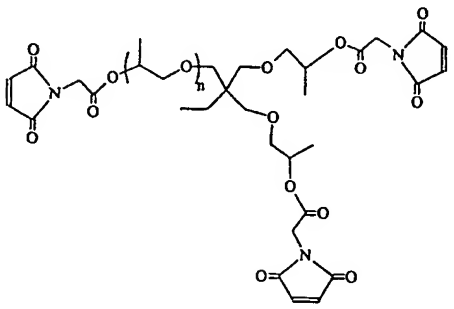


4.85g (25mmol) tetraethyleneglycol was dissolved in 100ml THF. When 7.0ml (50mmol) triethylamine and tert. butyl catechol were added, the solution was cooled to <0°C. 8.7g (50mmol) of N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. After stirring overnight at room temperature the suspension was filtered and evaporated. Extraction with CH_2Cl_2/H_2O yielded 9.4grams (20mmol) of a dark brownish oil.

^{1}*H-NMR, CDCl$_3$* (δ/ppm): 6.75(s,4H); 4.25(t,8H); 3.65(q,12H)

Example XII

Preparation of a tris-maleimide from propoxylated trimethylolpropane



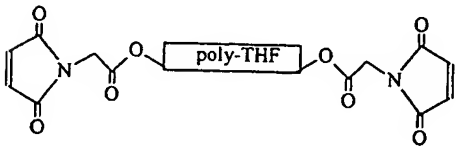
11.4g (37mmol) propoxylated trimethylolpropane (1PO/OH) was dissolved in 200ml THF. 9.1ml (112mmol) pyridine and tert. butyl catechol were added while the solution was cooled to -10°C.

19.5g (112mmol) N-[(chloroformyl)methyl] maleimide dissolved in 80ml THF was added dropwise over three hours. The reaction was stirred at room temperature during the night. After filtration the clear pink solution was washed two times water and with saturated NaCl. Drying on Na_2SO_4, filtration and evaporation resulted in a yellow oil with red spots in it. Dissolving in dichloromethane, filtration and evaporation yielded 20grams (27.8mmol, 75%) of a yellow oil.

^{1}H-NMR, $CDCl_3$ (δ/ppm): 6.85(s,6H); 5.0(m,3H); 4.2(s,6H); 3.3(m,12H); 1.3(m,2H); 1.15(d,9H); 0.775(t,3H)

Example XIII

Preparation of an α,ω-hydroxy polytetrahydrofuran-650 functionalised with two maleimide end groups

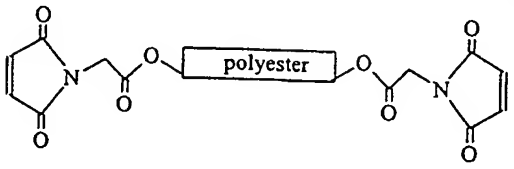


12.85g (20mmol) α,ω-hydroxy-polyTHF-650 was dissolved in 125ml THF. 6.0ml (43mmol) triethylamine and tert. butyl catechol were added while the solution was cooled to -10°C. 7.0g (40mmol) N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added in 45 minutes. After stirring overnight at room temperature, filtration and evaporation the oil was extracted with ether/H_2O.

The product was collected as a orange oil with a yield of 8.4grams (9.1mmol, 45.4%).

Example XIV

Preparation of a bis-maleimide functionalised polyester

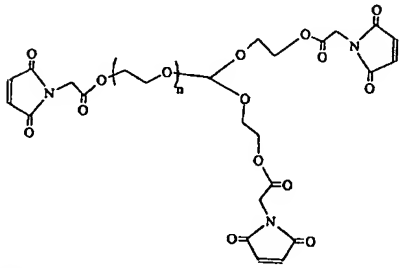


73g (43meq) hydroxyfunctional aromatic polyester (no ethylenical unsaturations) was dissolved in 250ml THF. 5.75ml triethylamine and tert. butyl catechol were added while the solution was cooled to 0°C. To the vigorously stirred solution N-[(chloroformyl)methyl]

maleimide dissolved in 50ml THF was added. The reaction was stirred overnight at room temperature evaporated and extracted with CH_2Cl_2/H_2O.
Over 50g of the polyester functional maleimide was obtained as a orange oil which contains a few percentages of high boiling aromatic solvent.

Example XV

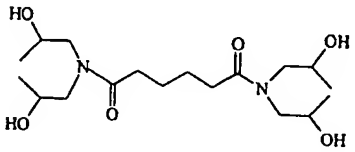
Preparation of a tris-maleimide from ethoxylated glycerol



14g (14mmol) ethoxylated glycerol, tert. butyl catechol and 7.0ml (50mmol) triethylamine were dissolved in 150ml THF and cooled to -10°C. N-[(chloroformyl)methyl] maleimide dissolved in 50ml THF was added dropwise. The reaction was filtered and evaporated after stirring overnight at room temperature. The dark residu was extracted with CH_2Cl_2/H_2O and 12.9g (9mmol,64%) of a dark brown oil was obtained.

Example XVI

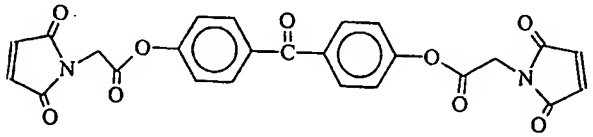
Tetra-maleimide from m-Primid®



4.7g (12.5mmol) m-Primid® (see formula) was suspended in 100ml chloroform. 7.0ml (50mmol) triethylamine and tert. butyl catechol were added. The well stirred mixture was cooled to 0°C and 8.7g (50mmol)N-[(chloroformyl) methyl] maleimide dissolved in 60ml $CHCl_3$ was added dropwise over two hours. After the reaction was stirred overnight at room temperature no amine hydrochloric acid salts were precipetated. Extraction with water yielded 10g (10.8mmol, 86%) of a green/yellow oil.

Example XVII

Preparation of 4,4' bis-maleimide benzophenenone

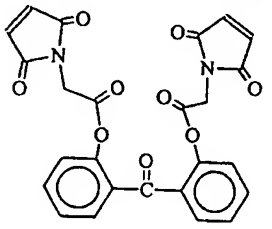


5.35g (25mmol) of 4,4-dihydroxybenzophenone was dissolved in 195ml THF. Triethylamine (7ml) tert. butyl catechol were added and the mixture was cooled to -20°C. N-[(chloroformyl)methl]maleimide (8.7g, 50mmol), dissolved in 50ml THF was added dropwise. The reaction

mixture was stirred overnight at room temperature. The white suspension was filtered, the filtrate was evaporated and the obtained white-light rose powder was dried and pulverized to yield 3.7g product.

Example XVIII

Preparation of 2,2' bis-maleimide benzophenone



In an analogous way to example XI starting with 2,2'-dihydroxybenzophenone, the compound aimed at was obtained. After the overnight reaction, the solvent was removed by N_2-flow, and the red solution was filtered and the filtrate evaporated. The so obtained oil was dissolved in 200 ml CH_2Cl_2, and the salmon-rose solution was extracted twice with 40ml 10% HCl, and four times with 40ml H_2O. After drying and evaporation of the solvent, 4.4g product was obtained.

Example XIX

Preparation of a bis-maleimide from hydroxy functional, hydrogenated polybutadiene

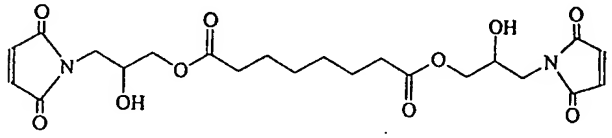
Hydrogenated polybutadiene 1.19 meq/g OH, Mw = 1000 (21g) was dissolved in 300ml THF and cooled to -10°C after addition of 5 ml triethylamine and tert. butyl catechol. The N-[(chloroformyl)methyl] maleimide (5g), dissolved in THF was slowly added dropwise. After

stirring overnight at room temperature and filtration, the filtrate was evaporated, dissolved in CH_2Cl_2 and extracted with 30ml H_2O.

After drying and evaporating, the product was obtained as an orange oil in an amount of 12g.

Example XX

Reaction of the epoxy maleimide with a di-acid (bis-maleimide from suberic acid)



Suberic acid (2.6g) and epoxymaleimide (4.6g) were dissolved in 100 ml $CHCl_3$.

The reaction was catalysed using $Et_4N^+Br^-$. Stabiliser was tert. butyl catechol. The reaction mixture was refluxed for 4 hr, and thereafter was left stirring over the week and at room temperature. The mixture was refluxed for a few hours, cooled, some residue was filtered of and the filtrate was evaporated to yield 6g product.

Use of maleimide compounds of Ex.XII, X, XVII, VII, VIII and XIV respectivally in a radiation curable composition:

- A radiation curable composition was prepared by mixing 2 wt.% of the compound obtained in example XII with 98 wt.% of a tetrafunctional polyesteracrylate

(Ebecryl®80 from UCB).

A coating was applied on a glass substrate using a 150 µm K-bar and the coating was cured by UV light (1 J/cm^2, using a Fusion H-bulb lamp under N_2 atmosphere.

A test specimen was cut from the cured film (3x4 cm), and acetone extractables were measured by 24 hr extraction in 100 ml acetone. The weight of the sample was measured before and after extraction, and the weight loss determines the amount of extractables.

To determine the type of extractable compounds, the acetone was evaporated and the residue was analysed with 200 MHz ^{1}H-NMR. From this analysis, the ratio of acrylate functional extractables and non-acrylate extractables could be determined.

The cured coating did have 4 wt.% of extractables, which were mainly acrylates. Only about 0.1 wt.% or less was non-acrylate, which means that only about 5% of the photoinitiator appeared to be extractable.

In contrast, if the same acrylate resin is cured with 2 wt.% of Irgacure 184 (a type-I photoinitiator), the cured coating exhibited 5 wt.% of extractables, of which 1.2 wt.% originated from the photoinitiator (hence, 60% of the photoinitiator appeared to be extractable from the cured product).

In case the same acrylate resin was cured using a conventional type II initiating system (benzophenone with an amine synergist), also 60% of the photoinitiating system appeared to be extractable.

- Coating compositions were prepared with 1 wt.% of the triethyleneglycol bismaleimide of example X, 1 wt.% of

N-methyl diethanolamine and 98% of acrylate (Ebecryl P-36, 80, 83 or 810) according to Table 2. Coatings were prepared and cured as described above. The König hardness was measured, results are given in Table 2.

Table 2

Resin*	König hardness(s) of coating**
Ebecryl® P-36	9.8
Ebecryl® 80	74.2
Ebecryl® 83	26.6
Ebecryl® 810	32.2

* Ebecryl® 36: 86% acrylated oligomer; 14 wt.% diethylene glycol diacrylate
Ebecryl® 80: amine modified polyether acrylate (tetrafunctional)
Ebecryl® 83: amine modified polyether acrylate (tetrafunctional)
Ebecryl® 810: polyester acrylate

** coating: 1 wt.% Ex. X + 1 wt.% N-methyldiethanolamine + 98 wt.% resin*

- The compound of Example XVII was used in 1 wt.% with 99 wt.% Ebecryl 83, curing with 1 J/cm^2 resulted in a coating with a Köning hardness of 81 s.

- The Maleimide compounds (1 wt.%) given in Table 3

were mixed with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% Ebecryl®80.

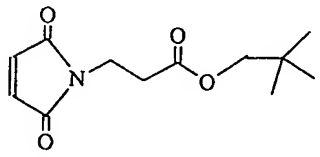
Table 3

Maleimide From	König(s)
Example VII	74.2
Example XIII	57.4
Example XIV	46.2

Examples XXI and XXII are related to the preparation and characterisation of a monofunctional maleimide compound with more than 1 methylene spacer group between the maleimide group and the functional group and to the preparation of a radiation-curable composition comprising said maleimide.

Example XXI

Preparation of a monofunctional maleimide from neopentyl alcohol:



40 mmol 2,2-dimethyl-1-propanol was dissolved in 175 ml dry tetrahydrofuran. 40mmol triethylamine and tert-butyl catechol were added. The mixture was cooled to 0°C and 40 mmol N-[(chloroformyl)ethyl]maleimide dissolved in 50 ml tetrahydrofuran was slowely dropped to the solution. The reaction mixture was stirred overnight at room

temperature. After filtration and evaporation, a pale orange liquid residu was obtained. Cooling in a cold aceton bath, and drying in a vacuum oven yielded 30.7 mmol of a solid product.

Example XXII

Preparation of a radiation curable composition comprising a maleimide compound:

A radiation curable composition was prepared by mixing 1 wt.% of the maleimide compound of Example I with 1 wt.% of N,N-dimethylethanolamine and 98 wt.% of an tetrafunctional polyester acrylate oligomer (Ebecryl®80 from UCB).

A coating was applied on a glass substrate using a variable thickness doctor blade, wire wound applicator (e.g. a 200 µm 'K-bar') and the coating was cured by UV light (N_2, 2.2 J/cm^2), using a Fusion H-bulb lamp.

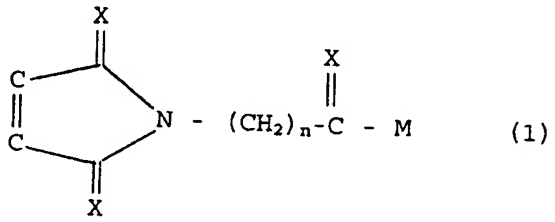
The cured coating exhibited a König hardness of 65.8 s.

This shows that the presence of such a maleimide compound in a coating composition results in a radiation-curable coating, which is properly cured upon radiation.

CLAIMS

1. Process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (1)



(1)

wherein M is halogen or alkoxylate, and each X, independently, is O or S, with

a compound (2) comprising a backbone and having at least 1 group per molecule, capable of reacting with the compound according to formula (1), and

(ii) obtaining the maleimide compound.

2. Process according to claim 1 wherein the maleimide compound is monofunctional.

3. Process according to claim 2 wherein n is equal to 1 and wherein said backbone is not comprising benzophenone, a succinimide or a phenyl group.

4. Process according to claim 2 wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 169 and is not comprising an anhydride or cyclodextrine group.

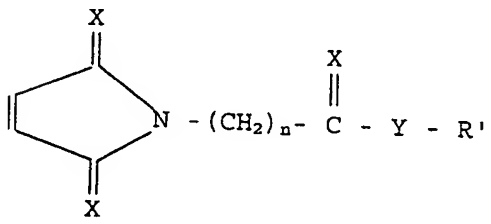
5. Process according to claim 1 wherein the maleimide compound is multifunctional.

6. Process according to claim 5 wherein n is equal to 1.

7. Process according to claim 5 wherein n is greater than 1 and wherein said backbone has a molecular weight higher than 150 and does not comprise a nitrogen containing phenyl group.

8. Process according to any one of claims 1-7 wherein each X is oxygen.

9. Monofunctional maleimide compound according to formula (6)



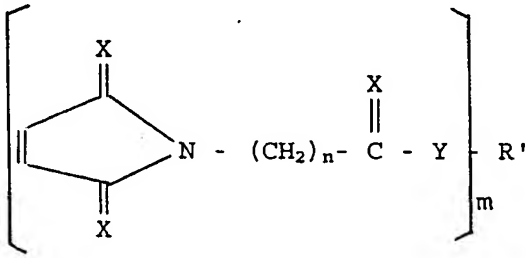
(6)

wherein Y is O, S or NH; each X, independently, is O or S; and R' is the remainder of the backbone, and wherein
(i) n equals 1 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and not comprising benzophenone, a succinimide or anhydride group, or
(ii) n equals 2 and R' is an organic backbone comprising hydrogen, carbon and at least one of O, S, or N, and said backbone is not comprising a diol-substituted alkane, a succinimide, anhydride or cyclodextrine group, or
(iii) n is at least 3.

10. Monofunctional maleimide compound according to claim 9 wherein the molecular weight of the monofunctional maleimide compound is from about 159 to about 100,000.

11. Monofunctional maleimide compound according to any one of claims 9-10 wherein the molecular weight of the monofunctional maleimide compound is from about 173 to about 10,000.

12. Multifunctional maleimide compound according to formula (7)



(7)

wherein Y is O, S or NH, R' is the remainder of the backbone, and m is - on average - 1.6 or higher, and wherein

(i) n equals 1 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons, or

(ii) n is at least 2 and R' comprises a hydrocarbon backbone having a molecular weight higher than 150, an (oligo)ether, (oligo)ester, (oligo)carbonate, (oligo)urethane, (oligo)imide, (oligo)amide, (oligo)acrylate backbone, or mixtures thereof and wherein said backbone is not comprising an alicyclic group having two hydroxyl groups on adjacent carbons.

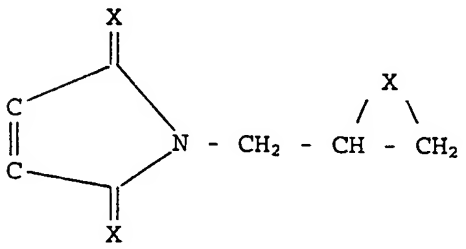
13. Multifunctional maleimide compound according to claim 12 wherein the compound has a functionality

of 1.9 or higher.

14. Multifunctional maleimide compound according to any one of claims 12-13 wherein the molecular weight of the maleimide compound is from about 250 to about 100,000.

15. Process for the preparation of a maleimide compound comprising the steps of

(i) reacting a compound according to formula (3)



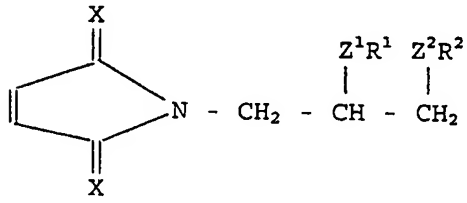
(3)

wherein X, independently, is O or S, with

a compound (4) having at least on average 1 group per molecule, capable of reacting with the compound according formula (3) and

(ii) obtaining the maleimide compound.

16. Maleimide compound according to formula (8)



(8)

comprising at least one maleimide group, wherein X is O or S, and Z^1 and Z^2 independently designate for O, S, or NR^3, and wherein R^1, R^2 and R^3 can be, independently, hydrogen or an organic group and

wherein at least R^1 or R^2 is the remainder of the molecule.

17. Radiation-curable composition comprising

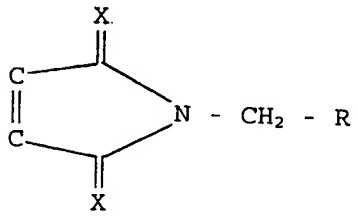
a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)

b) at least one maleimide compound according to any one of claims 9-14 or 16.

18. Radiation-curable composition comprising

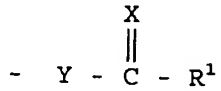
a) at least one compound having ethylenically unsaturated bonds other than those in maleimide groups as defined under (b)

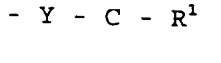
b) at least one multifunctional maleimide compound having on average at least 1.6 maleimide groups according to formula (9)



(9)

wherein R is





wherein

each X, independently, is O or S

Y is O, S or NH, and

wherein R^1 is the remainder of the backbone of the multifunctional maleimide compound.

19. Composition according to any one of claims 17-18

wherein the composition comprises conventional photoinitiators or photosensitizers, or mixtures thereof.

20. Product coated with a cured coating which coating before curing is a coating composition according to any one of claims 17-19.